

19



Europäisches Patentamt
European Patent Office
Office européen des brevets



11 Publication number:

0 274 387 B1

12

EUROPEAN PATENT SPECIFICATION

- 43 Date of publication of patent specification: 16.09.92 51 Int. Cl.⁵: **B01D 69/12, B01D 71/38, C07C 51/41, C07C 227/00, //C23C18/38**
- 21 Application number: **88100110.1**
- 22 Date of filing: **07.01.88**

54 Alkali resistant hyperfiltration membrane.

30 Priority: **08.01.87 US 1488**

43 Date of publication of application:
13.07.88 Bulletin 88/28

45 Publication of the grant of the patent:
16.09.92 Bulletin 92/38

64 D signated Contracting States:
BE DE FR GB IT NL

59 References cited:
EP-A- 0 114 286
EP-A- 0 192 310
DE-A- 2 730 528
JP-A-61 268 302

PATENT ABSTRACTS OF JAPAN, vol. 10, no. 31 (C-327)[2088], 6th February 1986

73 Proprietor: **FILMTEC CORPORATION**
7200 Ohms lane
Minneapolis Minnesota 55435(US)

72 Inventor: **Cadotte, John E.**
5637 Scenic Drive
Minnetonka Minnesota 55345(US)

74 Representative: **Casalonga, Axel et al**
BUREAU D.A. CASALONGA - JOSSE Moras-
sistrasse 8
W-8000 München 5(DE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

This invention relates to membranes useful to separate solutes or dispersed materials having relatively low molecular weights from higher molecular weight materials.

Porous membranes for separation of minute particles, typically one to ten μm in diameter, from a liquid medium are known. U.S. Patent 4,279,752 describes microporous polyvinyl alcohol membranes prepared by forming membranes containing silica and then extracting the silica. U.S. Patent 4,073,733 discloses porous polyvinyl alcohol membranes prepared by dissolving polyalkylene glycol in polyvinyl alcohol and coagulating the polymer from the solution.

Crosslinked water-soluble polymers are used as an ultra-thin solute barrier in a composite membrane disclosed in U.S. Patent 4,559,139. These membranes are useful for separation of potable water via reverse osmosis from brackish water.

U.S. Patent 3,852,388 describes a variety of techniques for making microporous membranes. Phase inversion is a particularly popular technique for making such membranes, but the practical lower limit for the molecular weight discrimination of such membranes is generally 500 or greater.

Japanese Kokai 54-118,697 describes a method for making a porous membrane useful to treat body fluids. In this method, a polyvinyl alcohol hollow fiber is coagulated in a caustic solution and then treated with glutaric aldehyde and sulfuric acid to effect crosslinking of the polyvinyl alcohol.

JP-A-86/268302 as published in Patent Abstracts of Japan vol.11 no. 132 (April 24, 1987) or in Chem. Abstracts vol.106, no.16 (April 20, 1987), discloses an aromatic polysulfone membrane prepared by dissolving polysulfone and poly(ethylene glycol) in N-methyl-2-pyrrolidone. The composition was spun into hollow fibers, soaked in aqueous 6% poly(vinyl alcohol), dried and soaked in an aq. solution containing sulphuric acid and glutaric aldehyde for water-insolubilization.

Membranes have been proposed and studied for use in the treatment and reprocessing of industrial by-products. One of the deficiencies of prior art ultrafiltration membranes are that the commercially available polyamide and polyester membranes are not durable in high pH applications. Membranes having improved chemical stability and separation characteristics are actively being sought for use in membrane processes for treating liquids.

The present invention concerns a novel hyperfiltration membrane and process for making the membrane. The hyperfiltration membrane comprises a porous support layer and a discriminating layer affixed to the porous support. The discriminating layer comprises a plurality of pores in a matrix of a water-compatible polymer which has been rendered normally water-insoluble by crosslinking or other means.

The present invention thus relates to a hyperfiltration membrane comprising

(a) a porous support layer; and

(b) affixed to the support layer, a discriminating layer having a plurality of micropores in a normally water-compatible polymer matrix which bears a plurality of groups reactive with aldehyde, said polymer being crosslinked via reaction of a difunctional or polyfunctional aldehyde to render the polymer normally water-insoluble.

The membrane is characterized in that

- (i) the cross-linking reaction has been carried out in the presence of a phosphorus-containing acid, and
- (ii) the membrane exhibits a water flux of at least $70.8 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$ (15 gfd) and a rejection of at least 60 percent when tested with an aqueous solution of 0.2 percent of a first compound or salt having a molecular weight in the range from 300 to 1,000 at 200 psi (1379 kPa) and 25°C , with the sum of the water flux in gfd and rejection of the first compound or salt in percent equal to at least 90; and
- (iii) the membrane exhibits a NaCl rejection of less than 30 percent when tested with an aqueous solution of 0.2 percent NaCl at 200 psi (1379 kPa) and 25°C .

Advantageously, the difference between the NaCl rejection and the rejection of the first compound or salt as determined in the aforementioned tests is at least 50 percent. The recovery for purposes of the aforementioned tests is typically 1 percent.

In another aspect, the invention is a process for making a hyperfiltration membrane. This process comprises first coating at least one major surface of a porous support with a solution comprising a water-compatible polymer bearing at least two -OH, -SH, primary amine, secondary amine or amide groups bearing reactive hydrogens. The coating solution further comprises a crosslinking agent selected from the group consisting of di- or polyfunctional aldehydes, ketones bearing two or more keto groups and activated vinyl compounds bearing at least two moieties reactive with the reactive hydrogens of the polymer and said crosslinking agent is present in an amount effective to render the polymer normally insoluble in water at temperatures in the range from 20° to 50°C . The coating solution also includes: (1) an acid which is a solvent or swelling agent for the water-compatible polymer and is normally present in the liquid phase at

conditions of coating, and (2) a solvent for the water-compatible polymer. The coating solution is then dried and heat cured so as to crosslink the water-compatible polymer, resulting in a membrane with the aforementioned water flux and rejection of a first compound of a molecular weight greater than 300 and the aforementioned rejection of NaCl. The acid should be relatively non-volatile, pore-forming when leached out and relatively uniformly dispersed in the coating layer.

In yet another embodiment of this invention, the membranes described herein are used to separate monovalent sodium salts from complex polyvalent sodium salts. This membrane is particularly useful in processing solutions from an electroless copper plating process to recover EDTA (ethylene diamine tetraacetic acid) salts. Electroless copper plating processes are well known, see, e.g., U.S. Patent 3,475,186. The membrane described herein is much more permeable to formaldehyde and sodium formate than to copper EDTA or sodium EDTA. A solution from a copper-plating process contacting the feed side of the membrane under pressure or some other chemical potential difference will promote selective permeation of sodium formate and formaldehyde through the membrane, leaving a reject stream of concentrated sodium and copper EDTA salts. The concentrated EDTA salts can be readily recycled to the electroless process.

In preferred embodiments of this invention, the resulting membrane exhibits a water flux of at least $236 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$ (50 gfd) and a rejection of at least 98 percent when tested at 600 psi (4137 kPa) and 25°C for copper EDTA (copper salt of ethylene diamine tetraacetic acid) with an aqueous solution prepared from 1 percent $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 2 percent Na_4EDTA at a pH 12. The NaCl rejection is preferably less than 20 percent when tested with an aqueous solution of 0.2 percent NaCl at 200 psi (1379 kPa) and 25°C . All percentages are by weight unless otherwise indicated.

The term "hyperfiltration" is used herein to denote a pressure-driven membrane process for removal of dissolved inorganic and organic constituents from a liquid solution by selective transport of certain components of the liquid through the membrane. The term "water-compatible polymer" is used herein to refer to polymers soluble to an extent of at least 0.5 weight percent, more preferably at least 2 weight percent at 25°C in water or aqueous solutions containing from 1 to 50 weight percent of C_1 to C_4 alkanols, C_2 to C_4 alkylene diols or polyols or other water-miscible low molecular weight solvents. "Normally water-insoluble", as used herein, refers to a composition which is substantially insoluble in water at temperatures below 50°C , although some components present may be extractable.

Preferred first compounds or salts used to determine the rejection and flux of the subject membranes are Na_4EDTA for hyperfiltration membranes and dextran or polyethylene glycol for membranes having a higher molecular weight cut-off.

In a preferred embodiment, subject membranes are useful in the separation of solutes having a molecular weight of 100 or less from solutes having a molecular weight of 300 or more. In certain preferred embodiments, the membranes are useful for separation of by-products present in aqueous feeds at a pH of 11 or 12. For example, these membranes can be used to separate iron salts of ethylene diamine tetraacetic acid from sulfate or sulfite salts, as would occur in nitrogen oxide removal from stack gases. The molecular weight cut-off can be raised by use of higher acid concentrations and the resulting membrane used as an ultrafilter or foul-resistant coating for ultrafilters. The membranes are operable as foul-resistant separators for liquid hydrocarbon oils from water. The membrane can also be used to remove impurities from alkaline solutions, e.g., colored impurities or "color bodies" present in caustic solutions.

The subject hyperfiltration membranes are composite membranes having a porous support layer with an adherent discriminating layer. Composite membranes are known in the art. See, for example, U.S. Patents 4,559,139 and 4,277,344.

The porous support layer can be present in the configuration of a flat sheet, hollow fiber or tubular membrane. The pores in the surface of the support layer to be coated preferably range in size from 20 to $1,000 \text{ \AA}$, (2 to 100 nm) more preferably 50 to 500 \AA , (5 to 50 nm) as determined by scanning electron microscopy. Operable support layers are commercially available and can be made from a variety of polymers including polysulfone, polyvinyl chloride, polycarbonate, polyolefin and polyvinylidene fluoride. Porous supports which tolerate pH in the range from 1 to 13 are preferred. Porous polysulfone supports in a normally wet condition are particularly preferred. Generally, the porous support layer will include a fibrous backing or webbing on which the polymer forming the support was cast.

It is also operable, but not preferred, to use an inorganic support, such as glass, sintered metals or ceramics.

Generally, a major surface of the support layer will be coated with a discriminating layer. In some embodiments of the invention, pretreating the substrate with a surfactant or other agents may be desirable prior to coating. "Major surface", as used herein, refers to a surface of the support layer presenting a significant portion of the support's total surface area and which can be secured so that the major surface separates a first space from a second space. For example, a flat sheet support can be coated on one side with a

discriminating layer and then used in a spiral or plate and frame membrane device. A hollow fiber can be coated down either in the lumen of the fiber or on the external surface of the fiber. Optionally, more than one major surface of a support can be coated with a discriminating layer, but this is not generally desirable. Typically, the discriminating layer will be in direct contact with the fluid feed.

5 The support layer is coated with a solution containing a water-compatible polymer, a crosslinking agent and an acid, where said acid both catalyses crosslinking and contributes to pore formation in the crosslinked polymer. Any convenient technique known in the prior art can be used to apply the coating. For example, the support can be dipped in, sprayed with or wiped with the coating solution. After coating the surface, excess liquid is conveniently removed with a roller or via conventional techniques. Desirably, the
10 coating should be as thin as possible, while still maintaining its integrity. In general, the flux through the discriminating layer is inversely proportional to its thickness. Preferably, the discriminating layer, after drying, is in the range from 500 to 5,000 Å (50 to 500 nm) thick, more preferably 1,000 to 2,000 Å (100 to 200 nm).

The solvent used for the coating solution is preferably water. Lower (C_1 to C_3) alkanols, polyethers, polyols or other similar organic solvents are also operable as solvents or co-solvents, provided that the
15 water-compatible polymer, crosslinker and acid are soluble in the solvent to the desired concentration and the solvent does not deleteriously affect the reaction of the polymer with the crosslinker. Co-solvents, surfactants or other additives may be desirable in minor amounts to decrease foaming, enhance film-forming or improve other properties of the coating solution.

20 Water-compatible polymers are preferably those exhibiting good chemical stability and desired membrane characteristics. Illustrative polymers include acrylamide polymers, cellulosic polymers bearing a plurality of hydroxyl groups, polyethyleneimine and other polymers or copolymers which bear reactive hydrogen moieties and which are water-compatible. Particularly preferred polymers are vinyl polymers bearing a plurality of hydroxyl groups, such as partially or substantially completely hydrolyzed polyvinyl
25 acetate and vinyl acetate copolymers. Monomers which can operably be used in the vinyl acetate copolymers include crotonic acid and acrylic acid. Polyvinyl alcohol or a vinyl acetate polymer or copolymer which has been hydrolyzed to the extent necessary to render the polymer water-compatible are especially preferred. More preferably, the polymer is a polyvinyl alcohol which is 75 to 96 percent hydrolyzed, most preferably 88 percent hydrolyzed.

30 Preferred water-compatible polymers can be dissolved in an aqueous solution in a concentration of at least 1 weight percent. To this polymer solution can be added 1 weight percent phosphoric acid without coagulation or precipitation. This acid-containing polymer solution, when dried, will appear as a single phase film with no separate acid phase visible to the unaided eye.

The molecular weight of the polymer is generally not critical, so long as the polymer is water-compatible and will readily coat as a film on the support layer. Optimum molecular weights may vary
35 depending on the polymer, the substrate and solvent. If a polymer of a particular molecular weight is preferred in an embodiment of this invention, this can readily be determined empirically. Generally, polyvinyl alcohols having a molecular weight in the range from 10,000 to 125,000, as determined by gel permeation chromatography, are preferred in aqueous coating solutions. The molecular weights used herein
40 are number average molecular weights.

The water-compatible polymers used in the coating solutions must be rendered normally water-insoluble after coating. Preferably, the water-compatible polymer in the coating is reacted with a crosslinking agent to render it water-insoluble.

The crosslinking agents used herein are compounds bearing at least two substituents reactive under
45 acid pH conditions with the active hydrogen groups of the water-compatible polymer. Compounds bearing a plurality of aldehyde groups, such as glyoxal, glutaraldehyde, formaldehyde derivatives and the like, or bearing a plurality of ketone groups, such as 1,4-cyclohexanedione, are operable. Preferred crosslinking agents are glyoxal and glutaraldehyde. The crosslinking agent should produce a degree of crosslinking effective to render the water-compatible polymer normally water-insoluble.

50 The acid present in the coating solution should be essentially non-volatile and should not crystallize at the conditions of coating and drying. The acid should be sufficiently compatible with the water-compatible polymer to swell or dissolve the polymer. Operable acids include phosphorus-containing protic acids of various oxidation states, with phosphoric acid being preferred. Of course, compounds which will form phosphoric acid in aqueous solutions are also operable, such as polyphosphoric acid. Illustrative acids
55 include hypo-, meta-, ortho- and pyro-phosphorous acid and hypo-, meta-, ortho- and pyro-phosphoric acid.

The acid is believed to serve as a pore-forming agent. It appears likely that some polyphosphoric acid is formed during curing, but the invention herein is not so limited. Optionally, other leachable pore-forming agents can be used in addition to the acid, but generally are not desirable.

The acid pore-forming agent will itself catalyze the crosslinking reaction. When low temperature crosslinking is desired, additional catalysts can be used. Carboxylic acids incorporated in the polymer coating may also catalyze the crosslinking reaction, but in general do not possess significant catalytic activity. Sulfuric acid, trifluoromethylsulfonic acid, copper salts and zinc salts are operable as co-catalysts.

5 The co-catalysts can undesirably increase the rejection by the membrane of monovalent salts or sulfate salts.

The relative concentrations of the components present in the coating solution can be varied over a fairly wide range. The maximum and minimum concentrations conveniently used will vary dependent upon the solvent, polymer, cure temperature and other parameters used and components present. Because of the
10 viscosity of the solution and thickness of the cured coating at high concentrations of polymer, the polymer is preferably present at a level of less than 10 parts by weight, more preferably less than 5 parts by weight and most preferably less than 2 parts by weight. For convenience in removal of solvent during drying of the coating solution and to form films with good integrity, it is preferable that the solution contain at least 0.1 part by weight, more preferably at least 0.5 part by weight and most preferably at least 1 part by weight
15 polymer.

The weight ratio of acid pore-forming agent to polymer in the coating solution is preferably in the range from 1:2 to 20:1, more preferably 1:1 to 10:1 and most preferably 3:2 to 5:1. In general, pore size will increase with increasing concentrations of acid. Preferably, from 0.5 to 10 parts by weight, more preferably from 2 to 6 parts by weight, acid pore-forming agent is present in the coating solution. Even greater
20 concentrations of acid can be used if a higher molecular weight cut-off is desired. For example, a weight ratio of 8:1 of phosphoric acid to polyvinyl alcohol can be conveniently used to make an ultrafiltration membrane. Too high a concentration of phosphoric acid can be deleterious to formation of a dried sheet and membrane properties. The maximum operable acid concentration can be determined empirically.

The ratio of reactive sites on the polymer to reactive groups on the crosslinking agent is preferably in the range from 100:1 to 1:10, more preferably 20:1 to 1:5, in the coating solution. The degree of crosslinking generally is not believed critical, so long as the polymer is rendered water-insoluble. Pore size of the membrane product generally decreases with increasing amounts of crosslinking agent, at least until an
25 excess of the crosslinker is employed.

In one preferred embodiment of the invention, glyoxal is employed in the coating solution as a
30 crosslinking agent in a concentration of from 0.04 to 4 parts by weight, more preferably 0.1 to 2 parts by weight. In another preferred embodiment of the invention, glutaraldehyde is employed as a crosslinking agent in a concentration in the range from 0.025 to 1 part by weight, more preferably 0.05 to 0.5 part by weight. It should be noted that these aldehydes are volatile and some aldehyde may evaporate during the curing process.

35 If a low temperature cure is desired, a co-catalyst for the crosslinking reaction can be added to the coating solution. Operable co-catalysts include copper salts, zinc salts and other catalysts for the crosslinking reaction known in the art. Sulfuric acid is the preferred co-catalyst, when phosphoric acid is the principal pore-forming agent. From 0.01 to 2.0, preferably 0.1 to 1, parts by weight co-catalyst are generally desirable if a co-catalyst is used.

40 In a preferred embodiment of the invention, polyvinyl alcohol is used as the polymer with a glyoxal or glutaraldehyde crosslinking agent. Acetal groups are believed to be the predominant crosslink. In general, some hydroxyl groups will be present in the crosslinked polymer.

The coated support layer is dried at temperatures sufficient to promote crosslinking of the coating solution. Reduced pressures are operable during drying, but atmospheric pressure is generally convenient.
45 Depending upon the reactants, catalyst, concentration of reactants and heat resistance of the microporous support, temperatures in the range of from 60° to 150° C may be operable, with temperatures in the range from 90° to 120° C being generally preferred.

Porous substrate sheets commonly contain a non-woven backing on which they are cast. Some backing materials, such as polypropylene, may be adversely affected at high cure temperatures. Use of a co-
50 catalyst may permit lower cure temperatures, but care must be taken not to undesirably increase rejection by the membrane of low molecular weight materials.

The cure time generally will decrease as the cure temperature increases. Cure times in the range of from 1 to 30 minutes have been used with preferred coating solutions. The optimum time and temperature for curing a specific coating solution can be readily determined empirically.

55 The coating, after drying, is preferably washed or immersed in water to leach out the acid present in the coating. Alternatively, the acid can be leached out during the initial operation of the membrane.

The membranes of this invention can be fabricated by conventional techniques into membrane devices of configurations known in the art. Flat sheet membranes can be utilized in plate-and-frame or spiral

devices. Hollow fiber membranes and tubular membranes can be assembled in parallel or bias-wrap configurations known in the art. See, for example, U.S. Patents 4,080,296; 3,422,008 and 3,228,877. Spiral devices containing channel spacers and other components which will tolerate a pH of 12, are especially preferred.

The subject membranes can be used as supports for additional discriminating layers, if desired. Protective coatings or rejection enhancing coatings are also operable, but not preferred.

The membranes described herein can generally be operated over a wide range of feed solution compositions, pH ranges, transmembrane pressures and feed temperatures. A higher pressure of the feed side than the permeate side of the membrane is conveniently used as a driving force for transport through the membrane. The upper limit on transmembrane pressure is generally determined by the physical properties of the membrane. The lower limit on pressure is determined by the chemical potential difference required across the membrane. Transmembrane pressures in the range from 50 to 1,000 (345 to 6895 kPa), preferably 100 to 600 (689 to 4137 kPa), pounds per square inch gauge (psig) are generally preferred.

The operating temperature should be sufficiently high to maintain the feed and permeate in a fluid state. The upper limit on temperature is determined by the heat sensitivity of the components of the membrane device. Temperatures in the range from 0° to 50° C are generally convenient.

The pH of the feed solution can be any pH which the membrane and associated components will tolerate. The composition of the discriminating layer is advantageously selected, so as to tolerate the pH and composition of the feed solution. The preferred crosslinked polyvinyl alcohol coatings can tolerate a pH in the range from 6 to 13.

The membranes described herein are in general sufficiently porous that most of the water flux through the membrane occurs via flow through the pores. The pores are advantageously of a size such that chloride or sulfate salts of alkali metals pass through the membrane readily relative to higher molecular weight solutes or colloidal suspended materials which are rejected. Advantageously, the membranes are normally substantially non-ionic, i.e., the discriminating layer does not bear ionic groups at a pH of 7. Membranes can be made which are tolerant of pH 12 feed. These membranes also have utility in removal of oil emulsions from water, waste treatment processes and in processing of food.

The following examples are presented to illustrate but not otherwise limit the invention.

Preparation of Support Layer

A polyester non-woven fabric (from Filtration Sciences Corporation, sold as HOLLYTEX® 3329) was coated with a solution of 90 parts dimethyl formamide and 10 parts dimethyl sulfoxide containing 19.5 percent by weight of a polysulfone (Union Carbide UDEL® P3500 polysulfone) with a coating knife. The coated fabric was immediately quenched in water at 15° C. The film was cut into 6 inch by 12 inch (15 cm by 30 cm) pieces, secured to glass with adhesive tape and pressed with a hand roller to remove surface water.

Where the membrane is to be subject to high pH environments, a polypropylene non-woven fabric, such as VILEDON® FO 2430, available from Carl Freudenberg (Viledon Non-wovens Division), is preferred for the support layer. The polypropylene web can be coated in generally the same manner as the polyester.

Examples 1-4, Comparative Experiments A-B

Dilute aqueous solutions of polyvinyl alcohol (PVOH), phosphoric acid (H_3PO_4) and optionally glyoxal or sulfuric acid (H_2SO_4) were prepared as tabulated in Table I. The composition is indicated in weight percent. The polyvinyl alcohol was obtained from Air Products and Chemicals Inc. and was 99.3 percent hydrolyzed with a viscosity of 55 to 65 centipoise (55×10^{-3} Pa.s to 65×10^{-3} Pa.s) for a 4 weight percent solution at 25° C.

The solution was spread on the support layer affixed to glass. Excess solution was removed by pressing the coated support with a rubber hand roller. The glass plate with the coated support was placed in a 100° C forced air oven for the tabulated time.

The dried membrane was removed from the glass and placed in a plate and frame test apparatus of conventional design. The rejection and flux of the membrane was determined at 200 psi (1379 kPa) and 25° C for an aqueous solution containing 0.2 weight percent NaCl and one containing 0.2 percent Na_4EDTA .

The parameters and results are tabulated in Table I.

TABLE I

Example	Comp.* Experiment	Coating Composition (Weight Percent)				Cure (Minutes)	0.2% NaCl		0.2% Na ₄ EDTA	
		H ₃ PO ₄	PVON	H ₂ SO ₄	Glyoxal		$\frac{m^3/m^2/s}{(gfd)}$ ¹	Rej. (%)	$\frac{m^3/m^2/s}{(gfd)}$ ¹	Rej. (%)
-	A	5	1	-	-	15	4623.4 (99)	401.2 (85)	7	57
-	B	5	1	1	-	15	2974 (63)	3826 (56)	4	80
1	-	3.93	0.926	-	1.11	1	8587 (76)	2868 (78)	2	43
2	-	3.93	0.926	-	1.11	5	2721 (46)	8198 (42)	2	53
3	-	3.93	0.926	-	1.11	10	2403 (51)	1222 (40)	2	65
4	-	3.93	0.926	-	1.11	15	1369 (29)	1718 (25)	2	80

*Not an embodiment of this invention.
¹ (gfd) = $4.72 \times 10^{-7} m^3/m^2/s$

In Comparative Experiment A, the rejection of the Na₄EDTA was not as great as desired. The presence of H₂SO₄ in the coating of Experiment B undesirably increased the NaCl rejection. Examples 1-4 disclose membranes which exhibit excellent water flux and good rejection of polyvalent sodium salts without greatly increasing the rejection of monovalent sodium salts. The use of a crosslinker in Examples 1 and 2 provided a relatively low Na₄EDTA rejection because of the short cure times relative to Examples 3 and 4.

The membranes in Examples 1 and 2 would be more useful for separation of a higher molecular weight material than Na_4EDTA from a low molecular weight salt, such as NaCl . The resulting membranes generally have a higher rejection for copper EDTA salts than Na_4EDTA .

5 Example 5

In a manner generally similar to Example 4, an aqueous coating of 3.93 weight percent H_3PO_4 , 0.926 weight percent PVOH and 1.11 weight percent glyoxal was applied to a porous polysulfone support and dried at 90°C for 15 minutes. The polysulfone support in this instance was cast on a polypropylene non-woven web.

The resulting membrane was tested in a plate and frame apparatus. The water flux of the membrane was determined to be 81 gfd ($382 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$) and NaCl rejection was 12 percent, when the membrane was tested with a 0.2 weight percent aqueous solution of NaCl at 200 psi (1379 kPa) and 25°C . The water flux was 60 gfd ($283 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$) and Na_4EDTA rejection was 89 percent, when the membrane was tested with a 0.2 weight percent aqueous solution of Na_4EDTA at 200 psi (1379 kPa) and 25°C .

Example 6

In a manner generally similar to Example 5, except that 1 weight percent sulfuric acid was present in the coating solution, a polysulfone substrate was coated and dried. When the resulting membrane was tested with a 0.2 percent solution of NaCl at 100 psi (689 kPa) a water flux of 14.8 gfd ($69.8 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$) and a NaCl rejection of 21 was determined. The water flux and Na_4EDTA rejection with a 0.2 percent solution of Na_4EDTA at 100 psi (689 kPa) were 18.0 gfd ($85 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$) and 95.3 percent, respectively.

In a comparison with Example 5, it can be seen that the sulfuric acid catalyst resulted in a decreased water flux and increased salt rejection.

Examples 7-12

In a manner generally similar to Example 5, six porous polysulfone substrates were coated with an aqueous solution of 3.93 weight percent H_3PO_4 , 0.926 weight percent PVOH and 1.11 weight percent glyoxal. In additional experiments, 1 weight percent sulfuric acid was also present in the coating solution. The coated substrates were then cured for 15 minutes in a forced air oven at a temperature in the range from 90° to 120°C .

The flux and rejection of the resulting membranes were tested with aqueous solutions of either 0.2 percent NaCl or 0.2 percent Na_4EDTA at 100 psi (689 kPa). The cure temperature and membrane characteristics for each membrane are presented in Table II.

TABLE II

Example	Cure Temp. ($^\circ\text{C}$)	0.2% NaCl		0.2% Na_4EDTA	
		Flux $\text{m}^3/\text{m}^2/\text{s}$ (gfd)*	Rej. (%)	Flux $\text{m}^3/\text{m}^2/\text{s}$ (gfd)*	Rej. (%)
7	90	245.4×10^{-7} (52)	7	240.7×10^{-7} (51)	85
8	120	70.8×10^{-7} (15)	28	89.7×10^{-7} (19)	94
9	90	56.6×10^{-7} (12)	39	75.5×10^{-7} (16)	95
10	100	28.3×10^{-7} (6)	60	42.5×10^{-7} (9)	97
11	110	37.8×10^{-7} (8)	64	56.6×10^{-7} (12)	97
12	120	14.2×10^{-7} (3)	65	23.6×10^{-7} (5)	98

* (gfd) = $4.72 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$

The higher drying temperature in Example 8 decreased the flux and increased the rejection of the membrane relative to that obtained in Example 7. The presence of sulfuric acid in Examples 9-12 significantly increased the NaCl rejection even at a 90°C cure temperature. The resulting membrane in Examples 9-12 is as useful as a "loose" reverse osmosis membrane, i.e., a membrane with only a moderate sodium chloride rejection. Shorter cure times would have to be used with the sulfuric acid catalyst to obtain the desired membrane properties.

Examples 13-20

In a manner generally similar to Example 1, dilute aqueous solutions of 1 weight percent polymer, 3.9 percent phosphoric acid, 3.9 percent phosphorous acid or 7.8 percent phosphoric acid, 1.2 percent glyoxal crosslinker (except Example 16 which substituted 0.5 percent glutaraldehyde) were coated on a porous polysulfone support. The coated support was then heat cured at 100°C for 15 minutes. The polymers used were: (a) PVOH, (b) hydrolyzed 90/10 vinylacetate/methacrylic acid copolymer, (c) poly(2-hydroxyethyl methacrylate), (d) hydrolyzed 90/10 vinylacetate/crotonic acid copolymer and (e) a hydrolyzed vinylacetate/acrylic ester copolymer in which the unhydrolyzed copolymer is more than 50 percent vinylacetate (sold by Monsanto Company as Gelva® TS100).

The water flux in gfd and percent salt rejection were determined for (A) 0.2 percent NaCl at 200 psi (1379 kPa), (B) 0.2 percent Na₄EDTA at 200 psi (1379 kPa) and (C) a mixture of 1 weight percent Na₄EDTA and CuSO₄ · 5H₂O at 600 psi (4137 kPa). The reverse osmosis test results and other parameters for each membrane are presented in Table III.

TABLE III

Ex.	Polymer	Acid	RO Test Data					
			A		B		C	
			Flux ¹ (gfd)	Rej.	Flux ¹ (gfd)	Rej.	Flux ¹ (gfd)	Rej.
13	a	3.9% H ₃ PO ₄	40	22	41	94	102	99
14	a	3.9% H ₃ PO ₄ *	91	22	93	94	179	90
15	a	3.9% H ₃ PO ₃	44	26	41	92	134	98.6
16	a	3.9% H ₃ PO ₄	93	23	136	92	240	93
17	e	3.9% H ₃ PO ₄	164	9	113	86	180	81
18	b	3.9% H ₃ PO ₄	82	19	69	93	134	96.7
19	c	7.8% H ₃ PO ₄	26	15	22	88	51	84
20	d	7.8% H ₃ PO ₄	83	16	76	90	152	97

* 1 percent trifluoromethane sulfonic acid added.

¹ (gfd) = 4.72×10^{-7} m³/m²/s

The data presented in Table III confirms the low sodium chloride rejection and high rejection for Na₄EDTA displayed by the subject membranes.

Claims

1. A hyperfiltration membrane comprising
 - (a) a porous support layer; and
 - (b) affixed to the support layer, a discriminating layer having a plurality of micropores in a normally water-compatible polymer matrix which bears a plurality of groups reactive with aldehyde, said polymer being crosslinked via reaction of a difunctional or polyfunctional aldehyde to render the polymer normally water-insoluble, characterized in that
 - (i) the cross-linking reaction has been carried out in the presence of a phosphorus-containing acid, and
 - (ii) the membrane exhibits a water flux of at least 70.8×10^{-7} m³/m²/s (15 gfd) and a rejection of at least 60 percent when tested with an aqueous solution of 0.2 percent of a first compound or salt having a molecular weight in the range from 300 to 1,000 at 200 psi (1379 kPa) and 25°C, with the sum of the water flux in gfd and rejection of the first compound or salt in percent equal to at least 90; and
 - (iii) the membrane exhibits a NaCl rejection of less than 30 percent when tested with an aqueous solution of 0.2 percent NaCl at 200 psi (1379 kPa) and 25°C.
2. The membrane as described in Claim 1 wherein the polymer in the membrane discriminating layer is a vinyl addition polymer bearing a plurality of hydroxyl groups.

3. The membrane as described in Claim 1 wherein the discriminating layer is in the range from 500 to 5,000 Å (50 to 500 nm) thick.
4. The membrane as described in Claim 1 wherein the membrane is substantially non-ionic.
5. The membrane as described in Claim 1 wherein the NaCl rejection is less than 20 percent when tested with an aqueous solution of 0.2 percent NaCl at 200 psi (1379 kPa) and 25 ° C.
6. A process for making a hyperfiltration membrane comprising the steps of:
 - (a) coating at least one major surface of a porous support with a solution comprising:
 - (i) a water-compatible polymer bearing a plurality of -OH, -SH, primary or secondary amine or amide groups bearing reactive hydrogens; (ii) a crosslinking agent selected from the group consisting of di- or polyfunctional aldehydes, ketones bearing two or more keto groups and activated vinyl compounds bearing at least two moieties reactive with the reactive hydrogens of the polymer in an amount effective to render the polymer insoluble;
 - (iii) a phosphorus-containing acid which is a solvent or swelling agent for the water-compatible polymer and is normally present in the liquid phase at the conditions of coating in an amount effective to catalyze crosslinking and to form a plurality of pores in the coating when dried and
 - (iv) a solvent for the water-compatible polymer;
 - (b) drying the coating so as to crosslink the water-compatible polymer with the crosslinking agent.
7. The process as described in Claim 6 wherein the water-compatible polymer is a polymer or copolymer of vinyl acetate wherein at least 65 percent of the acetate groups have been hydrolyzed, or polyvinyl alcohol.
8. The process as described in Claim 6 wherein the phosphorous-containing acid is phosphorous acid, phosphoric acid or polyphosphoric acid.
9. The process as described in Claim 6 wherein the resulting membrane has a water flux of at least 15 gfd ($70.8 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$) and a rejection of at least 60 percent when tested with an aqueous solution of 0.2 percent Na_4EDTA at 200 psi (1379 kPa) and 25 ° C; and a NaCl rejection of less than 30 percent when tested with an aqueous solution of 0.2 percent NaCl at 200 psi (1379 kPa) and 25 ° C.
10. A process for separating alkali metal salts of a C_1 to C_4 carboxylic acid from salts of a chelating agent comprising:
 - (a) contacting the discriminating layer of a membrane as described in Claim 1 with an aqueous solution containing salts of the carboxylic acid and the chelating agent;
 - (b) effecting a chemical potential difference across the membrane so that salts of the carboxylic acid selectively permeate through the membrane;
 - (c) recovering the aqueous solution of carboxylic acid salts from the second surface of the membrane.

Patentansprüche

1. Hyperfiltrationsmembran, umfassend:
 - (a) eine poröse Trägerschicht; und
 - (b) an der Trägerschicht befestigt eine Trennschicht mit einer Vielzahl von Mikroporen in einer normalerweise wasserträglichen Polymermatrix, welche eine Vielzahl von mit Aldehyd reaktionsfähigen Gruppen trägt, wobei das Polymere über Reaktion eines difunktionellen oder polyfunktionellen Aldehyds, um das Polymere normalerweise wasserunlöslich zu machen, vernetzt ist, dadurch gekennzeichnet, daß
 - (i) die Vernetzungsreaktion in Anwesenheit einer Phosphor enthaltenden Säure durchgeführt worden ist, und
 - (ii) die Membran aufw ist:
einen Wasserdurchfluß von wenigstens $70.8 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$ (15 gfd) und eine Rückweisung von wenigstens 60 % beim Testen mit einer wässrigen Lösung mit 0,2 % einer ersten Verbindung oder eines ersten Salzes mit einem Molekulargewicht im Bereich von 300 bis 1.000 bei 200 psi (1379 kPa) und 25 ° C, wobei die Summe des Wasserdurchflusses in gfd und die Rückweisung

der/des ersten Verbindung oder Salz s in Prozent wenigstens gleich 90 ist; und
(iii) die Membran eine NaCl-Rückweisung von weniger als 30 % beim Testen mit einer wässrigen Lösung von 0,2 % NaCl bei 200 psi (1379 kPa) und 25° C aufw ist.

- 5 2. Membran nach Anspruch 1, worin das Polymere in der Membrantrennschicht ein eine Vielzahl von Hydroxylgruppen tragendes Vinyladditionspolymeres ist.
3. Membran nach Anspruch 1, worin die Trennschicht eine Dicke im Bereich von 500 bis 5.000 Å (50 bis 500 nm) hat.
- 10 4. Membran nach Anspruch 1, worin die Membran im wesentlichen nicht-ionisch ist.
5. Membran nach Anspruch 1, worin die NaCl-Rückweisung weniger als 20 % beim Testen mit einer Lösung von 0,2 % NaCl bei 200 psi (1379 kPa) und 25° C ist.
- 75 6. Verfahren zur Herstellung einer Hyperfiltrationsmembran, umfassend die Stufen des:
(a) Beschichtens wenigstens einer größeren Oberfläche eines porösen Trägers mit einer Lösung welche umfaßt:
(i) ein wasserverträgliches Polymeres, welches eine Vielzahl von -OH, -SH, primären oder
20 sekundären Amin- oder Amid-gruppen, die reaktionsfähige Wasserstoffatome tragen, besitzt;
(ii) ein Vernetzungsmittel, ausgewählt aus der aus di- oder poly-funktionellen Aldehyden, Ketonen mit zwei oder mehr Ketogruppen und aktivierten Vinylverbindungen, die wenigstens zwei mit den reaktionsfähigen Wasserstoffatomen des Polymeren reaktionsfähige Einheiten tragen, bestehen-
25 den Gruppe in einer zum Unlöslichmachen des Polymeren wirksamen Menge;
(iii) eine Phosphor enthaltende Säure, welche eine Lösungs-oder Quellmittel für das wasserver-
trägliche Polymere ist und normalerweise in der flüssigen Phase unter den Beschichtungsbedin-
gungen vorliegt, in einer zur Katalyse der Vernetzung und zur Bildung einer Vielzahl von Poren in
der Beschichtung beim Trocknen wirksamen Menge, und
(iv) ein Lösungsmittel für das wasserverträgliche Polymere;
30 (b) Trocknens der Beschichtung, so daß das wasserverträgliche Polymere mit dem Vernetzungsmittel vernetzt wird.
7. Verfahren nach Anspruch 6, worin das wasserverträgliche Polymere ein Polymeres oder Copolymeres von Vinylacetat, in welchem wenigstens 65 % der Acetatgruppen hydrolysiert sind, oder Polyvinylalko-
35 hol ist.
8. Verfahren nach Anspruch 6, worin die Phosphor enthaltende Säure Phosphorsäure, phosphorige Säure oder Polyphosphorsäure ist.
- 40 9. Verfahren nach Anspruch 6, worin die erhaltene Membran einen Wasserdurchfluß von wenigstens 15 gfd ($70,8 \times 10^{-7} \text{ m}^3/\text{m}^2/\text{s}$) und eine Rückweisung von wenigstens 60 % beim Testen mit einer wässrigen Lösung von 0,2 % Na_4EDTA bei 200 psi (1379 kPa) und 25° C, und eine NaCl-Rückweisung von weniger als 30 % beim Testen mit einer wässrigen Lösung von 0,2 % NaCl bei 200 psi (1379 kPa) und 25° C aufweist.
- 45 10. Verfahren zur Trennung von Alkalimetallsalzen einer C_1 bis C_4 -Karbonsäure von Salzen eines Chelatierungsmittels, umfassend:
(a) Inkontaktbringen der Trennschicht einer Membran nach Anspruch 1 mit einer Salze der Karbon-
säure und des Chelatierungsmittels enthaltenden wässrigen Lösung;
50 (b) Herbeiführung einer chemischen Potentialdifferenz quer zur Membran, so daß Salze der Karbon-
säure selektiv durch die Membran durchdringen;
(c) Gewinnung der wässrigen Lösung der Karbonsäuresalze von der zweiten Oberfläche der Membran.

55 Revendications

1. Membrane pour hyperfiltration, comprenant
a) une couche poreuse de support, et

b) une couche discriminante fixée sur la couche de support, présentant un grand nombre d micropores au sein d'une matrice en polymère normalement compatible avec l'eau, qui porte un certain nombre de groupes réactifs vis-à-vis d'un aldéhyde, ledit polymère étant réticulé par réaction avec un aldéhyde difonctionnel ou polyfonctionnel, qui rend le polymère normalement insoluble dans l'eau,

caractérisée en ce que

- i) la réaction de réticulation a été effectuée en présence d'un acide phosphoré, et
- ii) la membrane présente un débit d'eau d'au moins $70,8 \cdot 10^{-7} \text{ m}^3/\text{m}^2 \cdot \text{s}$ (15 gfd), et un taux de rejet d'au moins 60 %, quand on lui fait subir un test avec une solution aqueuse à 0,2 % d'un premier composé ou sel présentant une masse moléculaire située dans l'intervalle allant de 300 à 1000, sous 200 psi (1379 kPa) et à 25 °C, la somme du débit d'eau, exprimée en gfd, et du taux de rejet du premier composé ou sel, exprimé en pour-cent, étant au moins égale à 90; et
- iii) la membrane présente un taux de rejet de NaCl inférieur à 30 %, quand on lui fait subir un essai avec une solution aqueuse à 0,2 % de NaCl, sous 200 psi (1379 kPa) et à 25 °C.

2. Membrane conforme à la revendication 1, dans laquelle le polymère présent dans la couche discriminante de la membrane est un polymère d'addition de type vinylique, portant un certain nombre de groupes hydroxyle.

3. Membrane conforme à la revendication 1, dans laquelle l'épaisseur de la couche discriminante vaut de 500 à 5000 Å (50 à 500 nm).

4. Membrane conforme à la revendication 1, et qui est pratiquement non-ionique.

5. Membrane conforme à la revendication 1, qui présente un taux de rejet de NaCl inférieur à 20 % quand on la teste avec une solution aqueuse à 0,2 % de NaCl, sous 200 psi (1379 kPa) et à 25 °C.

6. Procédé de fabrication d'une membrane pour hyperfiltration, comprenant les étapes consistant à :

(a) revêtir au moins une surface majeure d'un support poreux avec une solution comprenant :

- (i) un polymère compatible avec l'eau, portant un certain nombre de groupes -OH, -SH, amino primaire ou secondaire ou amide, comportant des atomes d'hydrogène réactifs ;
- (ii) un agent de réticulation choisi dans le groupe constitué par les aldéhydes difonctionnels ou polyfonctionnels, les cétones comportant deux groupes carbonyle ou plus, et les composés vinyliques activés comportant au moins deux fragments réactifs vis-à-vis des atomes d'hydrogène réactifs du polymère, en une quantité efficace pour rendre insoluble le polymère ;
- (iii) un acide phosphoré, qui est un agent de dissolution ou de gonflement pour le polymère compatible avec l'eau et se trouve normalement présent dans la phase liquide dans les conditions dans lesquelles s'effectue le revêtement, en une quantité efficace pour catalyser la réticulation et pour former un grand nombre de pores dans le revêtement lors du séchage, et
- (iv) un solvant pour le polymère compatible avec l'eau ;

(b) faire sécher le revêtement de façon à provoquer la réticulation du polymère compatible avec l'eau, par l'agent de réticulation.

7. Procédé conforme à la revendication 6, dans lequel le polymère compatible avec l'eau est un polymère ou un copolymère de l'acétate de vinyle, dont au moins 65 % des groupes acétate ont été hydrolysés, ou du poly(alcool vinylique).

8. Procédé conforme à la revendication 6, dans lequel l'acide phosphoré est de l'acide phosphoreux, de l'acide phosphorique ou de l'acide polyphosphorique.

9. Procédé conforme à la revendication 6, dans lequel la membrane obtenue présente un débit d'eau valant au moins 15 gfd ($70,8 \cdot 10^{-7} \text{ m}^3/\text{m}^2 \cdot \text{s}$) et un taux de rejet d'au moins 60 %, lorsqu'on effectue un essai avec une solution aqueuse à 0,2 % de Na_4EDTA , sous 200 psi (1379 kPa) et à 25 °C, et un taux de rejet de NaCl inférieur à 30 %, lorsque l'on effectue un essai avec une solution aqueuse à 0,2 % de NaCl, sous 200 psi (1379 kPa) et à 25 °C.

10. Procédé pour séparer des sels de métal alcalin d'un acide carboxylique en C_{1-4} d'avec des sels d'un agent chélatant, comprenant :

- (a) la mise de la couche discriminante d'une membrane conforme à la revendication 1 en contact avec une solution aqueuse contenant des sels de l'acide carboxylique et d'un agent chélatant,
(b) l'établissement d'une différence de potentiel chimique à travers la membrane, de sorte que les sels de l'acide carboxylique traversent sélectivement la membrane par perméation, et
(c) la récupération de la solution aqueuse des sels d'acide carboxylique, de l'autre côté de la membrane.

5

10

15

20

25

30

35

40

45

50

55